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Abstract

β -Methyl and β -ethyl substitution of silanols has been reported to give small acid weakening effects in an earlier experimental study. In this study, ab initio computations have been used to assess β -methyl and β -ethyl substitution effects and have demonstrated that such effects are very small. Such results contrast with the commonly accepted acid strengthening β -alkyl substitution effects first demonstrated in alcohols.

Disciplines

Chemistry

Comments

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Gas-Phase Acidity Computations of Silanols and Their Sulfur Analogs

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β -Methyl and β -ethyl substitution of silanols has been reported to give small acid weakening effects in an earlier experimental study. In this study, *ab initio* computations have been used to assess β -methyl and β -ethyl substitution effects and have demonstrated that such effects are very small. Such results contrast with the commonly accepted acid strengthening β -alkyl substitution effects first demonstrated in alcohols.

Introduction

We recently reported that β -methyl substitution in silanols decreased acid strength in contrast to β -methyl substitution in alcohols.¹ Methylsilanol, $\text{CH}_3\text{SiH}_2\text{OH}$, was shown to be less acidic than SiH_3OH by 1 kcal/mol using bracketing techniques. We suggested that the attenuation of acid strength by β -methyl substitution resulted from a relatively greater contribution of inductive over polarizability effects in the silanols.¹ In contrast, a recent paper by Grimm and Bartmess reported that $(\text{CH}_3\text{CH}_2)_3\text{SiOH}$ is more acidic than $(\text{CH}_3)_3\text{SiOH}$ by 4.5 kcal/mol, a result which they suggested arose because of the dominance of polarizability effects.² In this paper, we use *ab initio* computational methods to examine the effect of β -methyl and β -ethyl substitution on SiH_3OH and β -methyl substitution on SiH_3SH .

Computational Details

Ab initio calculations were carried out with the GAMESS, Gaussian 88, and Gaussian 90 programs.^{3,4} Molecular geometries were optimized using closed-shell restricted Hartree–Fock (RHF) self-consistent-field (SCF) calculations with a 6-31G(d)⁵ basis set [denoted RHF/6-31G(d)]. The geometries determined in this manner were verified to be minima by analytically calculating and then diagonalizing the matrix of energy second derivatives (Hessian). The Hessian is positive definite in all cases discussed here. A succession of increasingly sophisticated basis sets [from 6-31++G(d,p) to 6-311++G(2df,2pd)]⁶ were used to determine the gas-phase acidities and to evaluate the convergence of the predicted energetics. The relative energies for the reaction $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$ were determined using these basis sets, together with full fourth-order perturbation theory (MP4).⁷

Results and Discussion

Gas-phase studies give an accounting of how substituents fundamentally affect reactivity, since the complications that often accompany studies in condensed phase are absent.⁸ It is now widely accepted that gas-phase substitution effects help provide an understanding of reactivity at a fundamental level, even though that understanding is still incomplete.^{8–10} Various ideas about substituent effects were originally derived from condensed-phase studies before gas-phase studies became prevalent. For example, it was generally accepted that the solution acidity of alcohols $[\text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > (\text{CH}_3)_2\text{CHOH} > (\text{CH}_3)_3\text{COH}]$ was a reflection of a fundamental effect, namely, the acid weakening, electron-donating inductive effect of β -methyl substitutions.¹¹ Consistent with this interpretation was the enhanced basicity of *tert*-butoxide over ethoxide in solution.¹² Beginning in the late 1960s, however, Brauman and co-workers demonstrated clearly

that β -methyl substitution effects were more complicated.¹³ Brauman and Blair showed that the acidity ordering given above for the alcohols in the condensed phase was reversed from that observed in the gas phase.¹¹ They suggested that polarizability effects, which increase as β -methyl and β -ethyl substitution increases, are the dominant effects determining these alcohol acidities.

Extensive subsequent studies have resulted in a better understanding of gas-phase acidities and substituent effects.^{8–10} Taft has treated gas-phase substituent effects by defining substituent constants as weighted linear combinations of polarizability, resonance, and inductive contributions.^{8,10} An explanation of the gas-phase acidity ordering of the alcohols in terms of Taft's treatment would suggest that the polarizability effects are large, while resonance and inductive effects are comparatively small. Since polarizability effects are generally so dominant in the gas phase, we have come to expect that they always dominate gas-phase acidities when alkyl substitutions are made. It is this notion that we examine here for both silanols and silanethiols.

Silanols. The gas-phase acidities of a number of silanols were recently reported.¹ These measurements were carried out using bracketing methods in a tandem selected ion flow tube flowing afterglow instrument. In particular, we determined the acid strength of a series of β -methyl-substituted silanols analogous to the alcohol series: SiH_3OH , $\text{CH}_3\text{SiH}_2\text{OH}$, $(\text{CH}_3)_2\text{SiOH}$, $(\text{CH}_3)_3\text{SiOH}$. The first of these was reported to be 1 kcal/mol more acidic than each of the others [$\Delta G^\circ_{\text{acid}} = 352$ kcal/mol for SiH_3OH and 353 kcal/mol for $\text{CH}_3\text{SiH}_2\text{OH}$, $(\text{CH}_3)_2\text{SiOH}$, and $(\text{CH}_3)_3\text{SiOH}$].¹ In contrast, the alcohol series spans a 6 kcal/mol range. We also reported an acid strength of 352 kcal/mol for $(\text{CH}_3\text{CH}_2)_3\text{SiOH}$. Although β -methyl and β -ethyl substitution effects on acid strengths of these silanols are very small, such effects in other silanols are somewhat larger.¹ Thus, $\text{C}_6\text{H}_5\text{SiH}_2\text{OH}$, $\text{C}_6\text{H}_5(\text{CH}_3)(\text{H})\text{SiOH}$, and $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiOH}$ have $\Delta G^\circ_{\text{acid}}$ values of 348, 350, and 353 kcal/mol, respectively, clearly indicating that β -methyl substitution decreases acid strength in this series. Although polarizability effects outweigh inductive effects in the alcohol series, the opposite is possible in the β -methyl-substituted silanols, since polarizability effects have an r^{-4} distance dependence, while inductive effects^{1,8,9} vary as r^{-2} . We have suggested that in silanols, where the Si–C and Si–O bond distances are both about 0.2 Å longer than the corresponding C–C and C–O bonds in alcohols, the acid weakening β -methyl inductive effect becomes more important than the polarizability effect because it operates with relatively greater effect with distance.¹

Because bracketing experiments are limited by the number of reference acids which can be used to establish the relative acid

TABLE I: Calculated (MP4) Gas-Phase Acidities (kcal/mol) of Silanols and Silanethiols

basis set	ΔE^a				
	SiH ₃ OH	CH ₃ SiH ₂ OH	CH ₃ CH ₂ SiH ₂ OH	SiH ₃ SH	CH ₃ SiH ₂ SH
6-31++G(d,p)	366.0	367.0	366.0	344.1	344.1
6-311++G(d,p)	366.9	367.9		345.1	346.3
6-311++G(2d,2p)	363.5	365.0		342.3	343.2
6-311++G(2df,2pd)	364.4			341.6	
$\Delta G^\circ_{\text{acid}}$	350.0 ^b			329.0 ^b	
	350.7 ^c	351.7 ^c	350.7 ^c		

^a ΔE is the change in energy for the process $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$ taking place at 0 K. ^b Using ΔE from MP4/6-311++G(2df,2pd) and adding scaled (0.89) zero-point vibrational energy corrections leads to the $\Delta H^\circ_{\text{acid}}$ values of 357.0 and 336.0 kcal/mol for SiH₃OH and SiH₃SH (at 0 K). These have been converted to the $\Delta G^\circ_{\text{acid}}$ values shown using a $T\Delta S$ estimate of 7 kcal/mol.²¹ ^c Using ΔE from MP4/6-31++G(d,p) and adding scaled (0.89) zero-point vibrational energy corrections leads to the $\Delta H^\circ_{\text{acid}}$ values of 357.7, 358.7, and 357.7 kcal/mol for SiH₃OH, CH₃SiH₂OH, and CH₃CH₂SiH₂OH (at 0 K). These have been converted to the $\Delta G^\circ_{\text{acid}}$ values shown using a $T\Delta S$ estimate of 7 kcal/mol.²¹

strength of an unknown acid, acidity determinations by equilibrium or collision-induced dissociation (CID) methods are preferred.^{14–16} Equilibrium methods generally fail for the silanols, however, since the simplest silanols themselves are unknown as isolable compounds. We have attempted to carry out CID experiments on the “complex” formed from H₃SiO[−] and (CH₃CH₂)₃SiOH with no success. The resulting CID products suggested that the “complex” was not a hydrogen-bonded one as required for this analysis.¹⁷ Rather, it appeared to be covalently bonded.

A recent paper by Grimm and Bartmess reported that (CH₃CH₂)₃SiOH is a stronger gas-phase acid than (CH₃)₃SiOH by 4.5 kcal/mol.² The acidities of (CH₃CH₂)₃SiOH and (CH₃)₃SiOH were determined using equilibrium and bracketing methods, respectively. Ours¹ and the Grimm and Bartmess² study agree quite closely on the absolute value of the acidity of (CH₃CH₂)₃SiOH but disagree on the acidity of (CH₃)₃SiOH. Although the experimental uncertainties in the two studies accommodate the results, there is a difference in the trends observed and their interpretation. Thus, Grimm and Bartmess indicate that an ethyl-for-methyl substitution leads to an increase in acid strength in silanols. This result is consistent with the dominance of polarizability effects in other gas-phase acidities. As indicated earlier, our results suggest that polarizability effects are attenuated in silanols and that inductive effects, which are acid weakening, contribute in a relatively greater, although small, way.

Because of the questions raised by these two studies and because the CID experimental approach failed, we sought an alternative way to analyze the magnitude and direction of β -alkyl substitution effects. As a result, we have undertaken an *ab initio* computational study of SiH₃OH, CH₃SiH₂OH, and CH₃CH₂SiH₂OH at levels of computational power which can evaluate small β -alkyl substituent effects. The results, which show the variation in energy with basis set for the general reaction $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$, are summarized in Table I. At the highest level of theory used for each silanol [MP4/6-311++G(2df,2pd) for SiH₃OH and MP4/6-311++G(2d,2p) for CH₃SiH₂OH], only small variations with basis set are observed. For SiH₃OH, there is only a 2.5 kcal/mol variation in going from the 6-311++G(d,p) to the 6-311++G(2df,2pd) basis set. Similar small changes hold for CH₃SiH₂OH. Comparison of our computations on SiH₃OH with those of Ahlrichs,¹⁸ Curtiss,¹⁹ and their co-workers shows a close correspondence. Thus, Sauer and Ahlrichs¹⁸ using the coupled pair functional method with an extended basis set predict a $\Delta H^\circ_{\text{acid}} = 359.3$ kcal/mol at 298 K. Our value for silanol is 357.0 kcal/mol at 0 K (correction to 298 K gives 356.6 kcal/mol). Curtiss, Brand, Nicholas, and Iton¹⁹ using G2 theory obtain a corresponding $\Delta H^\circ_{\text{acid}}$ of 356.2 kcal/mol at 0 K. All of the computations agree closely with our experimentally determined value of $\Delta H^\circ_{\text{acid}} = 359$ kcal/mol for SiH₃OH (at 298 K).¹ Thus, the validity of the *ab initio* computational approach for silanols is established for such high-level basis sets.

The data also demonstrate that variations with β -alkyl substitution are small, in the range 2–3 kcal/mol. More

importantly, the relative change in these energies due to a β -methyl substitution is almost unaffected by basis set. The effect of β -methyl substitution at high basis levels is shown to be small and in the direction found by our bracketing experiments. Nevertheless, we suggest only that such β -methyl substitution effects are small. In a similar manner, we have carried out MP4/6-31++G(d,p) level computations for CH₃CH₂SiH₂OH to show no effect for β -ethyl substitution. The similar result of this silanol to that of CH₃SiH₂OH studied at the same level of theory suggests that the effect of β -alkyl substitution by either methyl or ethyl is quite small. Further basis set enhancements for CH₃CH₂SiH₂OH would likely not alter this conclusion, since the relative acidities appear to be essentially basis set independent. All of our experimental and computational results, thus, present the consistent picture of very small β -alkyl substitution effects in silanols. Furthermore, these results suggest to us that the 4.5 kcal/mol acidity difference between (CH₃)₃SiOH and (CH₃CH₂)₃SiOH reported by Grimm and Bartmess is inconsistent with our results, although we are unable to explain the inconsistency.

Silanethiols. We have also carried out computational studies of SiH₃SH and CH₃SiH₂SH (see Table I) to assess β -methyl substitution effects in these closely related compounds. The effect of a β -methyl substitution using the 6-311++G(2d,2p) basis set is very small. This result is in the same order and of the same magnitude as a β -methyl substitution of silanol. When zero-point vibrational corrections and $T\Delta S$ estimations are included, the predicted $\Delta G^\circ_{\text{acid}}$ for SiH₃SH is 329 kcal/mol. A recent computational paper on silanethiols has appeared in which the results are obtained at far lower levels of theory than those reported herein.²⁰

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